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ROLLING MILLS: AN INDUSTRIAL WASTE GUIDE TO STEEL ROLLING MILLS

Environmental Health Center
Cincinnati, Ohio

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ROLLING MILLS

An Industrial Waste Guide to Steel Rolling Mills

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FEDERAL SECURITY AGENCY
Public Health Service
Environmental Health Center
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AN INDUSTRIAL WASTE GUIDE TO STEEL ROLLING MILLS

There were 215 establishments in the United States engaged in rolling steel in 1947. In that year these plants rolled over 66 million tons of finished products. The mills are located in 28 states; over 70 percent of them being in six states, as follows: Pennsylvania 69, Ohio 39, Illinois 27, New York 12, Indiana 11, and California 10.

Liquid industrial wastes of the rolling operations are roll-cooling water, descaling water, and waste pickle liquor. The principal pollutional features of these wastes are suspended solids, oil, grease, acid, and soluble iron. The suspended solids are fine particles of iron oxide (mill scale) which are removed from the surfaces of the product in the process. Oil and grease enters the wastes from leaks around bearings and from oil coatings placed on products to protect their surfaces. The acid and soluble iron are contained in waste pickle liquor. Pickle liquor is the spent solution from the process of removal, by dilute solutions of inorganic acids in water, of oxides from surfaces of the metal.

The rolling mill descaling and roll-cooling wastes of all steel rolling mills in the United States are estimated to be 600 million gallons per day. These wastes as they are discharged from the usual scale pits are estimated to carry to the receiving waters 250 million pounds of suspended solids and 100 million pounds of oil and grease each year.

In 1950 the steel industry produced over 19 million tons per year of steel products requiring pickling. Accurate estimates of waste pickle liquor volume and concentrations are difficult to obtain. It is conservatively estimated that in current years over 55,000,000 pounds of acid and 100,000,000 pounds of iron are contained annually in waste pickle liquor.

A description of the process sufficient for general understanding of waste sources with emphasis on operations producing liquid wastes is presented in the first section of the guide, a subsequent section contains information on the volume and character of the wastes. In the last section measures which remedy or abate the liquid waste problems of the industry are discussed.

Description of Process

Steel products of uniform cross sections, such as plates, bars, beams, rails, pipes, and sheets, are formed in rolling mills. The process of shaping steel by rolling consists of passing the material between two rolls revolving at the same peripheral speed and in opposite directions, and spaced so that the distance between them is somewhat less than the height of the section entering them. Under these conditions, the rolls grip the piece of metal and deliver it, reduced in cross-sectional area and increased in length. Physical properties of the steel prohibit making the total deformation in one pass so that a number of passes in sequence and through several mills is necessary. Rolls of the different mills are of such shape and spacing that the rudimentary form of the steel is transformed to that of the desired product.

Steel reaches the rolling mill in the form of ingots which are relatively short castings from 5 to 9 feet long and weighing 5 to 15 tons. Most of the ingot tonnage is rolled into the intermediate forms of blooms, slabs, or billets in a mill which may be referred to as a primary mill. Slabs are oblong in cross-section, 2 to 6 inches thick by 24 to 60 inches wide. Blooms are square or slightly oblong, in the range 6 x 6 inches to 10 x 12 inches. Billets are mostly square, from 2 x 2 to 5 x 5 inches.

These forms are rolled to the finished product in finishing mills or are forged. The primary mill of a large number of mill arrangements supplies hot semi-finished products either directly or through reheating furnaces to adjacent mills producing other semifinished or finished products. Finishing mills are of four basic classes: (1) plate, sheet, strip, and tin plate mills; (2) rail and structural mills; (3) bar, rod, and wire mills; and (4) pipe and tube mills.

Construction and Operation of Rolling Mills

Types of Mills

The three principal types of rolling mills used for rolling of steel are referred to as two-high, three-high, and four-high mills. As a matter of clarity, attention is directed to the fact the term rolling mill is used to refer both to a single stand of rolls and to several such mills and auxiliary equipment which make up an entire plant. A two-high stand consists of two rolls, one above the other. In order to make a number of passes through one two-high mill the piece must either be returned to the feed side or the rolls must be reversed between passes. A few primary mills consist of two two-high mills, one following the other. The piece is returned to the feed side of the rolls after passing both mills.

A three-high mill has three rolls; reversal of movement of the piece is accomplished by mechanically lifting the piece from the bottom pass to the top pass which then rolls the piece in opposite direction to the original pass.

Four-high mills have four rolls; the top and bottom rolls are backing-up rolls used to reinforce the smaller working rolls. Often a number of four-high stands are closely spaced in one continuous line; such arrangements are known as tandem mills. A continuous mill consists of several stands of rolls arranged in tandem with each succeeding stand operating with roll surface speed greater than its predecessor so as to compensate for elongation of the piece being rolled. Reduction takes place as the piece makes one continuous pass through all stands. This type of mill is in very common usage for rolling strip, sheet, billets, bars, rods, etc. Guide, loop, and cross country mills are made up of several stands in particular arrangements and are used for rolling products of small section. Guide and loop mills have the rolls of the separate stands in line, that is, the stands are placed side-by-side. This arrangement is referred to as mills in train. The piece being rolled passes one stand, then is guided or looped in a 180° bend to the next and so on through all stands. The cross-country mill has its stands arranged in two parallel trains. These mills involve the continuous idea; the trains are placed far apart so that the piece leaves the first stand of rolls in one train then is fed to the first stand of the second train and so on back and forth between stands of the two trains. The universal mill is a combination of horizontal and vertical rolls usually mounted in the same stand.

Rolling Mill Accessories

Many of the accessories of rolling mills are common to all types of plants; essential parts include the mill drive, lead spindle, pinions and their housings, spindles and coupling boxes, shock bearings, screws and screw-down mechanism, edgers, front and back mill tables, manipulators and side guards, entering and delivering guides, and roll-changing devices. Figure 1 shows a diagram of a reversing blooming mill to aid in locating and comprehending some of these parts.

The lead spindle is the shaft which transmits the power from the drive to the pinions. The pinions are gears which divide the power transmitted by the lead spindle between the rolls. Spindles are used to connect the pinions with the rolls of the mill. A screw-down is used to position the rolls for each pass through the mill. It consists of screws extending through the housing, hydraulic or electric drives and bearings.

Edgers consist of two vertically mounted rolls and are used to give a rolled edge to the product. Front and back roller tables feed and receive the piece during each pass; they consist of rollers ranging in diameter from 12 to 21 inches and spaced 2 to 3 feet apart. The manipulator consists of a pair of side guards which are movable laterally over the front and back roller tables. Lifting fingers, operating between the individual table rolls, are incorporated in the manipulator; they serve to turn the piece. The side guards move the piece to the correct pass position and straighten it when necessary.

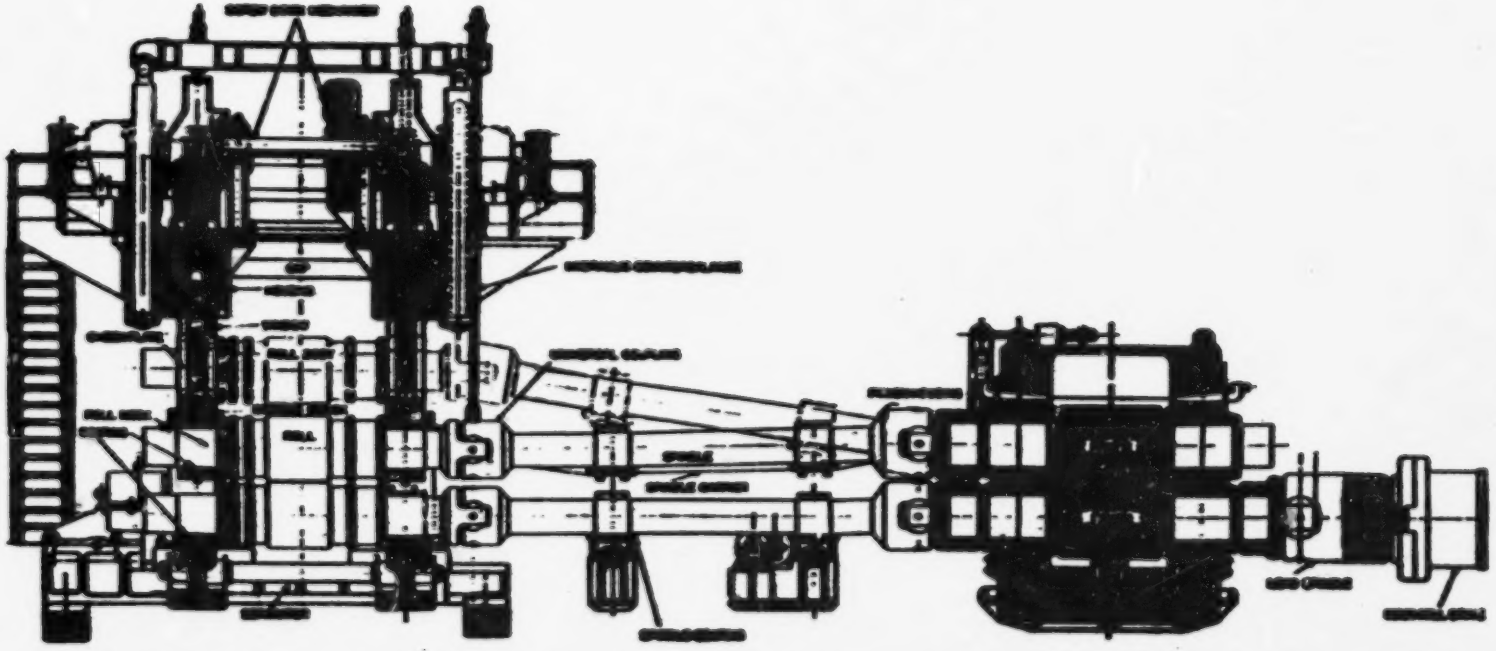

FIGURE 1- SCHEMATIC CROSS-SECTIONAL DIAGRAM OF A HYDRAULICALLY BALANCED HIGH-LIFT REVERSING BLOOMING MILL INDICATING LOCATION AND NOMENCLATURE OF PRINCIPAL PARTS.

Auxiliary Equipment

Major auxiliary equipment, of interest to this guide because of their operation being the source of liquid wastes, are discussed below.

(a) Shears and Saws

Shears are used to cut the two ends from the rolled piece and to cut the remaining piece into desired lengths. Construction of shears varies greatly with the type of piece being cut; as extreme examples, slab shears are massive knives moving vertically. Shears for sheet and strip are blades on a rotating drum which shear the piece as it travels. Structural shapes, rails and similar heavy shapes are cut with a revolving toothed blade, known as a hot saw, which combines mechanical sawing and melting of steel.

(b) Scale Breakers and Descaling

During periods when steel being rolled or heated is held at elevated temperatures, chemical compounds of iron and oxygen form on the surface of the steel. These oxides, known as mill scale, must be removed to prevent surface defects and wearing of dies and rolls. Removal of scale is accomplished within limits by scale breakers and hydraulic descalers. A scale breaker is a two-high mill in which very light reductions are made for initial breaking of the scale. Hydraulic descalers are high-velocity water sprays which are directed on the top and bottom surfaces of the heated metal as it leaves the scale breaker and at other points along the line of mills. Water pressures from 500 to 1500 psi are employed. The descaling action consists essentially in cracking-off, or loosening the scale from the sound metal by

sharp thermal contraction and the physical shattering of the loosened scale by the impinging force of the water jet. Prior to the introduction of modern hydraulic sprays expedient methods were used to get moisture between the work rolls and the stock where it vaporized instantaneously with explosive effects and removed the scale. Salt was commonly used as the moisture carrying agent. Moistened burlap was also employed. Some mills make use of these latter methods to some extent today.

Slab, Bloom, and Billet Mills

The first stages of forming useful products from ingots by hot rolling is accomplished in a primary mill. The ingots are first brought to a uniform temperature of about 2200°F. in a furnace called a soaking pit. An ingot buggy or travelling crane transfers a heated ingot from the soaking pits to the ingot receiving table which delivers it to the approach roller table. Front and back roller tables alternately feed and receive the piece during each pass through the rolling mill and manipulators rotate and move the piece as required. Five or seven passes usually produce a slab or bloom of the desired cross section. Primary mills of the two-high reversing type are most numerous. A variation of this form is known as a blooming and slabbing mill. It permits greater elevation of the top roll for edge passes of wide pieces. A third form known as the universal slabbing mill is provided with vertical rolls to perform the edge rolling. Three-high mills find use as ingot rolling mills where ingot sizes are very small.

In order to roll finished products of a small section with one heating, the mill rolling these sections must start with small billets. Hence, an intermediate mill between blooming and finishing mills is

required for rolling billets. Since blooms from 6 x 6 to 10 x 10 inches are usually taken from the blooming mill to the billet mill directly in one integrated operation without reheating, billet mills are often included in the primary mill classification. Reheating facilities between the blooming and billet mill are provided in the newer primary-mill installations.

Billet mills may be of the three-high, cross-country, or continuous types. The rolls of the three-high mill contain a series of grooves. Starting in the largest groove, the bloom is passed in turn through the others, becoming narrower and longer with each pass. A typical operation reduces a bloom 8 x 8 inches to a 4 x 4 inch billet in seven passes. Cross-country and continuous mills may contain as many as six stands. Continuous mills may have alternate horizontal and vertical stands.

Plate, Sheet, and Strip Mills

About 40 percent of rolled steel products now made in the United States are produced in these types of mills. Plate, sheet, and strip are distinguished from each other by differences in thickness and width. In general, plates are the thicker and heavier forms of thin flat products. The more light and wider forms are sheet and the narrow intermediate thicknesses in widths up to 12 inches are called strip.

Flat rolled products fall into two major categories: hot-rolled and cold-rolled. Hot-rolled products are reduced to final thickness at elevated temperatures throughout the process. Cold-rolled products are reduced to final thickness by rolling without heating, the major reduction having previously been accomplished while the product was hot.

Cold-rolled products are really cold-finished; however, the important distinction is that the products receive cold reduction in the final rolling operation.

Plate, sheet, and strip are produced by hot-rolling either from reheated slabs or slabs received directly from primary mills. Defects in the surfaces of slabs may be removed by one of several methods before the slab is reheated. Chipping, machining, and oxygen torch scarfing are all employed. In order that defects may be exposed, the scale on the outside surface may be removed by immersion of the steel in a dilute chemical solution, usually sulfuric acid. This process, termed pickling, is discussed in detail in a subsequent section of the report.

Slabs to be reheated for rolling are charged into the low temperature end of the furnace and progress toward the high-temperature end by being pushed progressively forward on water-cooled skids.

Some mills are designed to produce plate only; others produce sheet and strip as the finished product. By appropriate use of roll stands plate, sheet, and strip are all produced by certain mills.

Plate Mills

Plate-rolling mills are of various types including: (1) universal mills, (2) two-high mills, (3) three-high mills, (4) four-high mills, (5) tandem mills, (6) semicontinuous mills and (7) continuous mills.

A typical three-high plate mill is described as follows. This mill processes slabs ranging up to 44,000 pounds and produces plates from ¼ to 14 inches thick, 48 to 148 inches in width and up to 720 inches in length. Slabs are drawn from the furnace, placed on a transfer car and delivered to the mill approach tables which in turn deliver them to the tilting table. This table conveys the slab to

the mill and receives the stock at the elevation of the top pass on its return. The top and bottom rolls are 44 inches in diameter and the middle roll 28 inches. After seven or more passes, perhaps with some turning of the slab 90° to obtain width extension, the desired reduction is obtained. Scale is removed by spreading salt on the slab surfaces in the initial passes, followed by hydraulic descalers in later passes.

The plate is next conveyed from the three-high stand to a hydraulic spray which removes secondary scale and increases the cooling rates of heavy plates. The plate next passes through the leveller, thence to plate-marking equipment, and finally to the end and side shears.

Semi-continuous plate mills include a multipass, reversing, roughing unit coupled with two or more single-pass continuous finishing units. Two, three, and four-high stands are used as roughing units while several single pass four-high stands in tandem accomplish the finishing. Roughing units may include scale breakers, broadside stands, squeezers, and edgers. Broadside mills have long rolls so that the slab may be turned 90° and rolled crosswise to obtain width extension.

Strip Mills

In addition to producing sheet and strip, which are commercial terms designating the finished products as previously discussed, these mills produce a semifinished product known as "hot-rolled breakdowns" in coil form. Such coils are the starting material for the cold reduction process. These distinctions in product do not exist when the terms are used in connection with a continuous mill rolling such

products; thus, a mill rolling continuous lengths of strip, sheet or breakdowns commonly is known as a "strip mill."

A typical rolling train of a strip mill will consist of a roughing scalebreaker, four four-high roughing stands, a finishing scalebreaker, and six four-high finishing stands. Driven table rolls convey the steel from furnace to mill and from stand to stand. Figure 2 illustrates such a mill. For production of greater widths the mill may include a broadside mill and turntables for manipulating the slab. A slab squeezer also follows the broadside mill. A slab squeezer is a form of press which serves to true up slab edges and widths and to flatten them for subsequent rolling. Vertical rolls are provided integrally with the last three roughing stands. High-pressure hydraulic sprays to remove scale are located after the scale breakers and perhaps at several roughing stands.

Following the last finishing stand there is usually a flying shear for cutting the product into desired lengths. As the steel emerges from the last mill, it is carried over a long table called the runout table. Water sprays are often directed on the strip on the cooling table. Two or more coilers, located beneath the runout table, coil continuous long lengths when desired. Shorter lengths are stacked at the end of the runout table.

An alternate arrangement employs a reversing roughing mill and a continuous finishing train. A reversing mill may also be employed for finishing. Such a mill has a pair of pinch rolls and a coiler located on both sides (entry and exit) of the mill. The coils are placed inside small heating furnaces which keep the steel hot, permitting finishing to be carried out by repeated reversing of the

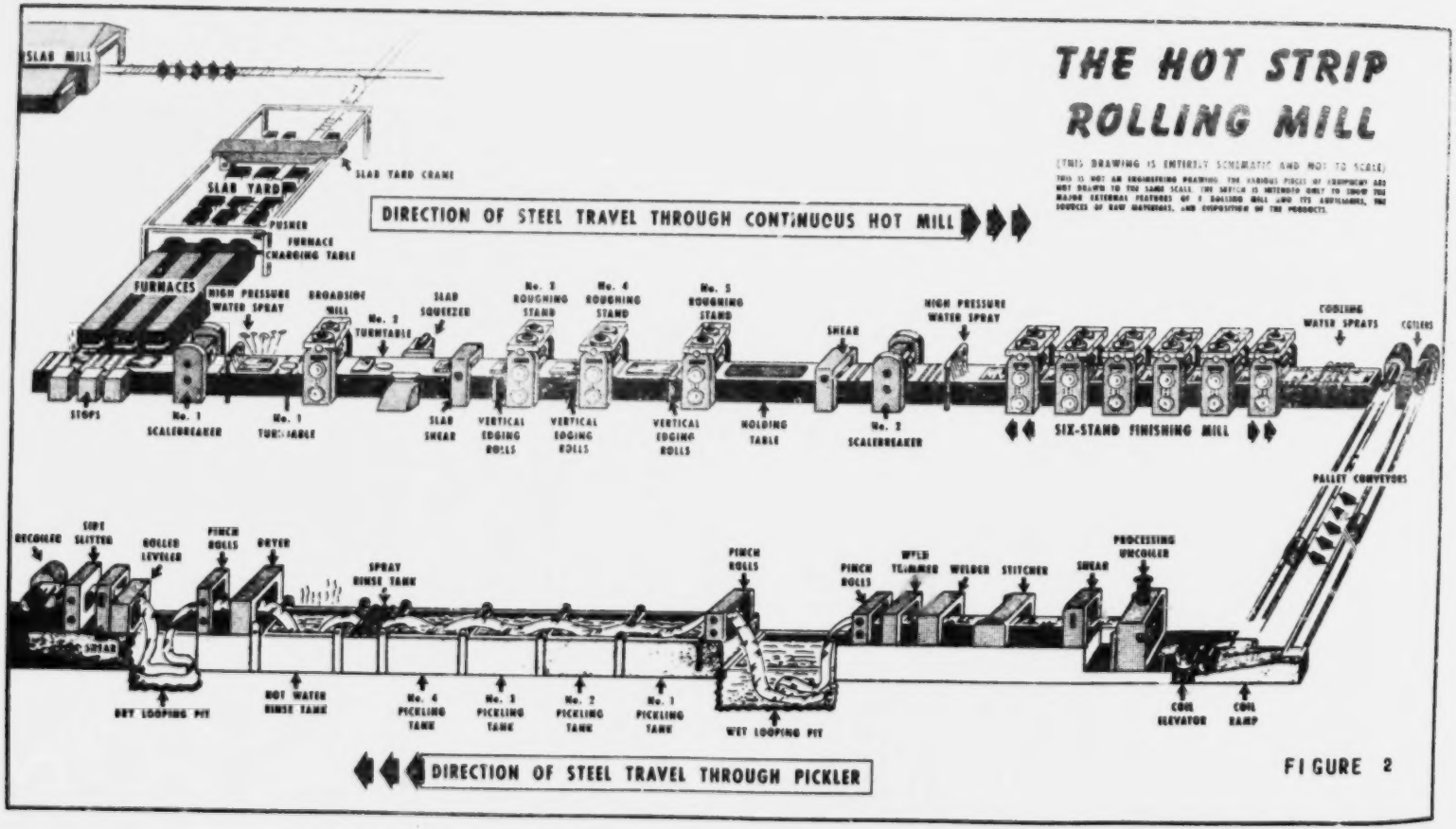
THE HOT STRIP ROLLING MILL
(THIS DRAWING IS ENTIRELY SCHEMATIC AND NOT TO SCALE)
SLAB MILL
SLAB YARD CRANE
SLAB YARD
PUSHER
FURNACE CHARGING TABLE
FURNACES
DIRECTION OF STEEL TRAVEL THROUGH CONTINUOUS HOT MILL
HIGH PRESSURE WATER SPRAY
BROADSIDE MILL
No. 2 TURNTABLE
SLAB SQUEEZER
No. 3 ROUGHING STAND
No. 4 ROUGHING STAND
No. 5 ROUGHING STAND
SHEAR
HIGH PRESSURE WATER SPRAY
COOLING WATER SPRAYS
COILERS
STOPS
No. 1 SCALEBREAKER
No. 1 TURNTABLE
SLAB SHEAR
VERTICAL EDGING ROLLS
VERTICAL EDGING ROLLS
VERTICAL EDGING ROLLS
HOLDING TABLE
No. 2 SCALEBREAKER
SIX-STAND FINISHING MILL
PALLEY CONVEYORS
UNCOILER
SIDE SLITTER
ROLLER LEVELER
PINCH ROLLS
DRYER
SPRAY RINSE TANK
PINCH ROLLS
PINCH ROLLS
WELD TRIMMER
WELDER
STITCHER
SHEAR
PROCESSING UNCOILER
SHEAR
DRY LOOPING PIT
HOT WATER RINSE TANK
No. 4 PICKLING TANK
No. 3 PICKLING TANK
No. 2 PICKLING TANK
No. 1 PICKLING TANK
WET LOOPING PIT
COIL ELEVATOR
COIL RAMP
DIRECTION OF STEEL TRAVEL THROUGH PICKLER

FIGURE 2

finishing stand.

Cold Reduction and Coating

Cold reduction consists of cold rolling hot-rolled breakdowns produced on the hot-strip mill, at temperatures generally between 150 and 250°F. The purposes of cold rolling are to reduce thickness (25 to 99 percent), to produce a smooth, dense surface and, with or without subsequent heat treatment, to develop controlled mechanical properties. Prior to cold rolling the oxide (scale) on the surface of the breakdown must be removed; this is usually accomplished by pickling, which is discussed in a subsequent section of the guide. Cold rolling is important in producing very thin flat-rolled steel, for instance, tin plate, all of which is produced by cold reduction, and sheet metal for auto bodies.

The coils of hot-rolled breakdowns are uncoiled, passed through a continuous pickler, dried, oiled, and re-coiled. The oil protects the coil from rusting and serves as a lubricant during cold reduction.

Cold reduction may be accomplished by continuous four-high stands with up to five units in tandem. Single reversing mills of the two-high or four-high types may also be used. These mills are characterized by their small diameter working rolls which are employed to obtain higher unit pressures. Heavy reductions at high speeds generate considerable heat that must be dissipated. This may be accomplished by a system of flood lubrication in which a water-soluble oil or a mixture of oils is directed in small streams or jets against the roll bodies and surfaces of the product.

Where flat sheet products are desired the coil may be taken to an uncoiling, side-trimming, and sheet-shearing line.

Following cold rolling the product is usually heat treated primarily to effect changes in mechanical properties which will render the material suitable for certain uses.

The lubrication film left on the product will decompose during heat treatment and leave undesirable residues of carbonaceous material, particularly if the sheet is to be coated. For this reason it is usually removed by strip cleaners employing alkaline detergent solutions. Cleaning systems employing the electrolytic principle are used at some plants. In such systems, detergent solution cleans the steel and serves as a conductor of current between electrodes and the products being cleaned. Thorough rinsing of the steel after cleaning is carried out to completely remove all contamination.

Cold rolled steel after heat treatment may be temper or skin rolled to impart the desired finish, to develop the desired mechanical properties, to increase steel hardness, and to produce acceptable flatness. The thickness reduction is held usually to less than 3 percent. Single-stand four-high mills may be used or two-stand tandem mills.

Sheets which are to be stored or shipped are oiled to prevent them from rusting. This is accomplished in an oiling machine which consists of a drip oil feed and oil spreading rolls.

An estimated 10 percent of rolled steel production of the United States is given a metallic coating for protection against corrosion. These coatings are of many kinds but tin and zinc are the predominate materials. For brevity, coating processes of these two materials only will be described.

A clean surface of the product being coated is essential. All rust, foreign material, and scale from hot rolling or annealing should

be removed from the steel before coating. Methods used include shot or sand blasting, pickling in acid, flame descaling, alkaline cleaning, and solvent degreasing.

Thin sheet is transformed into tinplate by coating the surfaces with tin by hot dipping, or electrolytically. A typical hot-dip tinning assembly includes (1) the feeder, (2) the tin pot and tinning machine, (3) the wet washing machine, (4) the branner, and (5) the piler. Sets of rolls convey the sheets through the molten flux floating on the tin bath into the molten tin then upward through a layer of palm oil in which are set three pairs of polished steel rolls. These help to remove excess tin and distribute the remainder evenly over the surface of the plate. The palm oil layer, in addition to protecting the surface of the molten tin bath from oxidation, tends to keep the tin coating on the sheet in a molten condition and thus allows the rolls to control the distribution and thickness of the tin layer. The tin-plated sheets are next passed through the wet washing machine. The purpose of this unit is to remove the excess palm oil from the surface of the coated sheet by means of a hot water solution of soda ash or trisodium phosphate. The solution at most plants is circulated from a storage tank which has a system for collecting the palm oil removed. The plates are then cleaned and polished by passing between a series of flannel disk rolls. Bran or middlings (a mixture of wheat and rye) are fed between the rolls to absorb moisture and distribute uniformly the oil from the washer that remains on the surface.

Electrolytic tin plating was extensively adopted during the last war because of reduced tin consumption. The plating is done by conducting a ribbon of strip steel through a tank containing a tin solution.

The passage of a direct electric current through the tank causes tin to be deposited on the steel. The equipment usually consists of an alkaline electrolytic cleaner, a rinsing unit, a pickler, another rinsing unit, a plating unit, a third rinsing unit, a fusion unit, a quench tank, a chemical treating unit, a fourth rinsing unit, a drying unit, an oiling unit, and finally a set of recoilers. It is the universal practice to melt and quench the electrodeposited tin to give it the brilliant luster typical of hot dipped plate. The chemical treating unit is for the purpose of providing a protective oxide film on tin plate. The plate is immersed or sprayed with a treating solution or the treatment may be electrochemical. Treating solutions used contain chromic acid or an alkali salt of chromic acid. Dilute solutions of sodium hydroxide carbonate, and phosphate and acid or alkaline chromate solutions are used in the electrochemical treatment.

Coating with zinc is termed galvanizing. The process resembles the hot-dipped tin plating process previously described. Sheets, lighter than 16 gage, to be coated are generally finished in cold reduction mills, but heavier galvanized sheets may be entirely hot rolled. In general the process includes oil cleaning, batch pickling, coating, cleaning, and shipping. The sheets or strip prepared for the coating line are first immersed in a muriatic acid solution, then conveyed through the coating bath of molten zinc, cooled, washed, dried, and levelled.

Roll and Structural Mills

The rolling of railroad rails and structural shapes such as I-beams, channels, angles, zee bars, sheet piling, and other special shapes is distinguished by the more complicated form of the sections as compared to simple rectangular forms produced on flat rolls. The rolls of rail and structural mills are carefully machined and accurately positioned so that a series of grooves or spaces between the rolls have such size and shape that the steel is caused to flow, spread, and bend to the desired section as it is rolled through the grooves. The transforming of the rectangular section of a bloom to that of a rail requires ten or more various shaped grooves each in turn gradually approaching the finished section desired.

Generally the production of structural shapes and railroad rails involves a number of processes as follows: heating of the bloom, rolling to proper contour and dimensions, cutting while hot to lengths that can be handled, cooling to atmospheric temperature, straightening, cutting to ordered lengths, inspecting, and shipping. A typical mill has a two-high reversing breakdown stand in which the initial shaping is accomplished, followed by a group of three stands, arranged in train, where the finishing process is completed. The first two of the three finishing stands are usually three-high. The finishing stand which is usually two-high, establishes the final shape of the rolled section.

The heated bloom is conveyed by the approach roller table to the first mill. Mechanical devices called manipulators align the bloom with the grooves of the first pass and turn it if necessary.

The rolls of the initial stands generally have 3 or more pass grooves. After making the required number of passes through the first groove the bloom is re-aligned by the manipulators for subsequent passes. The bloom after passing the initial stand is carried by the delivery table and tilting table to the next stand and so on through the finishing stand. The finishing stand rolls are generally limited to a single pass.

Bar, Rod, and Wire Mills

Bar mills produce round, square, or rectangular shapes of small cross section and such sections as window sash, small angles, fence posts, and small channels. One important product is reinforcing bars for concrete. Bar mills are often given the name merchant mill which term originated in reference to bar mills in the early days which carried a large selection of sizes from which merchants could select the size desired.

Bars are rolled from billets up to 5 x 5 inches in size. There are several types of bar mills; they usually consist of several stands of rolls. These mills, particularly the finishing stands are much less massive structures than mills previously described. Roll diameters are ordinarily 16 inches or less and roll lengths are short. A unique feature of early bar mills was the placing of several stands side by side with the rolls in one line. The product after passing one mill was looped around in a half circle and fed to the second mill and so on down the line. These mills are known as looping or guide mills. Some modern mills utilize continuous roughing mills with 8 or more stands in tandem and several finishing stands in train.

A bar mill may contain 16 or more stands. The most modern continuous bar mills have alternate horizontal and vertical rolls and finish the product in a continuous line of mills in tandem.

The finishing of bars may include straightening, surface conditioning, and heat treating. In order to prepare the bars for ultimate use or for inspection, the scale may be removed by pickling in weak acid solution. Pickled bars are usually dipped in rust preventive oil following pickling and drying.

The slender rods or bars from which wire is drawn are known as wire rod. The mills producing wire rod are similar to bar mills. Continuous tandem mills, continuous looping mills, and combinations of the two are employed. Continuous mills contain many stands, for instance, the working of billets into No. 5 rod (0.218 inch) requires 16 to 21 stands. Many mills have up to four rolling lines. Combination looping and tandem mills employ tandem mill roughing and looping mill finishing. Finished rod is coiled on reels.

The working of rods into wire is subject to much variation. The drawing operation consists essentially in drawing a rod through a tapered hole in some harder material, or successively through a series of such holes. The rod is pulled through the hole by a revolving block around which the rod winds. The dies are made with fluted approach, bringing about a gradual decrease in sectional area of the rod and a proportionate increase in length. In order to prepare the rod for drawing it is first given a number of preliminary treatments which vary according to the grade of steel, amount of drawing, and kind of finish desired. The first preliminary operation is that of cleaning; the scale and rust must be entirely removed before drawing,

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as otherwise, the holes in the dies would be quickly cut out of shape and the surface of the wire spoiled. The method generally employed for cleaning consists of pickling in hot dilute sulphuric acid. In drawing a rod through a die some sort of coating in addition to the die lubricant is imperative to prevent rapid wearing of the die. Several varieties of coatings are used including a water-rust coating, lime coating, and coating with copper or an alloy of copper and tin. Lime coatings are applied by dipping the coils in a vat containing milk of lime. The limed wire is baked in order to dry the lime and remove brittleness produced by the acid cleaning. Wire for most purposes is given some form of heat treatment following or during drawing.

Probably more than one-third of all steel wire is given some kind of metallic coating, either for decorative or protective purposes. Coating for protection against corrosion is principally galvanizing. The wire galvanizing process is similar to that for sheet metal which has been previously described.

Pipe and Tube Mills

Steel tubular products are manufactured by two methods, the welding process, and the seamless process. Welded tubular products are formed from sheets which are bent to circular form and the edges welded either by being forced together while hot or by electric or fusion welding. The long thin flat material from which force welded type pipe is formed is called skelp. This type of material may be rolled on sheet, strip, and flat bar bills previously described, yet, because of special features, skelp is best rolled by special mills.

In a typical mill a rectangular heated bloom is transformed to skelp by means of thirteen horizontal two-high stands and one vertical stand.

Fusion or electric welded tubing and pipe is first bent to circular shape from strip by means of a series of forming rolls, containing six to nine horizontal and four pairs of vertical rolls. The tube is then passed through a welding operation in which the edges are welded by the electrical resistance or fusion methods. Large diameter pipe may be fabricated from large plates which are bent in special crimping and bending machines and then welded.

Seamless pipes and tubes are manufactured from round billets 2 to 14 inches in diameter and up to 18 feet long by piercing a hole through the billet lengthwise and further refining the wall thickness and diameter in subsequent operations. Billets for making seamless pipe may be rolled directly from the product of blooming mills in two-high reversing bar mills. Diameters below 4 3/4 inches are produced by reheating small blooms and rolling on additional bar mills.

The operation of piercing is performed by two rolls whose axis of rotation are inclined to the axis of the piercing mandrel and whose faces are bevelled to form an angular entrance. The arrangement is best understood by reference to Figure 3. The rolls cause the metal

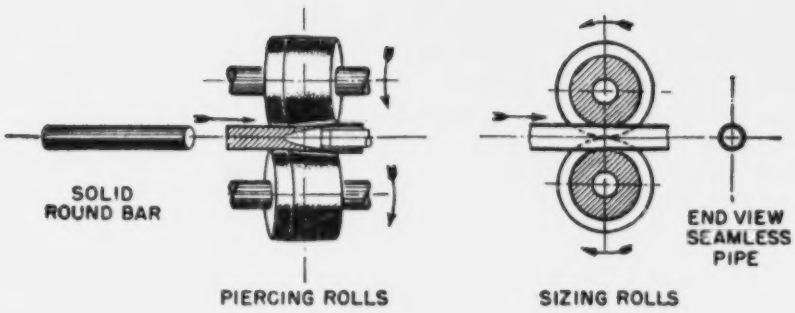

FIGURE 3 — SEAMLESS PROCESS

to flow over the nose of the piercer by the squeezing action from opposite sides which tends to make the steel draw part at the center thus providing space for the piercer to enter. As the steel moves on through the rolls, the piercer goes through the entire length of it forming a rough tube without any seam.

In order to meet requirements of greater accuracy, higher physical properties, better surfaces, thinner walls, and small diameters than can be produced by hot-working methods, hot-rolled tubes are cold drawn in an operation similar to the drawing of wire and cold rolling of sheets. In cold drawing, the tube is pulled through a tapered die of less diameter than the pipe. The tube is supported on the inside by a blunt-nosed mandrel while passing through the die, in order to effect wall thickness reduction and control the size of the hole. Prior to drawing, the pipe is pickled to remove scale, as described in a subsequent section.

Lubrication of Rolling Mills

Types of bearings and their lubrication are important to water pollution because of oil and grease losses to wastes. The bearings of working, backing-up, scale-breaker, and other rolls may be of two

general types; roller bearings or chock bearings. In the United States, adoption of roller bearings has been extensive since 1932. Roller bearings are now common in new mills, although they have not replaced entirely the chock type of bearing, which possesses the advantage of greater simplicity of construction. Roller bearings are lubricated by automatic greasing systems. Such a greasing system consists of a grease pump, piping connecting the pump to lubrication fittings on the equipment, and an automatic timer for actuating the pump at regular intervals.

Chock bearings consist of heavy metal castings lined with another material over the area in contact with the roll neck. The bearings inserts may be babbitt, brass, or bronze or they may be nonmetallic inserts of synthetic resin, lignum-vitae, or hard wood. Lubrication of metallic chock type bearings may be accomplished by a recirculating oil system. In such a system oil is pumped from a central storage tank to the bearings, passes through the bearings, and flows back to the collecting tank. Periodically the oil in the system may be purified by centrifuging and filtering. The construction and operation of a bearing for such a system is described as follows. Oil at 14 psi is distributed on the bearing through a series of ports along the top. Recesses along the sides of the bearing accumulate and distribute the oil on the face of the roller. Around the circumference at the edges of the bearing are close-fitting seal rings. Next outside the seal rings is a groove which is followed by another seal ring. Oil passing the first ring accumulates in the groove and flows by gravity to an oil storage tank from which it is recirculated. A special type of oil lubricated metallic bearing is the fluid-film bearing. These bearings

are fully enclosed; the inner and outer races are separated by an unbroken film of oil. The oil itself carries the load and distributes it over a large surface.

Synthetic-resin bearings are made of either canvas or belting fabric, impregnated with phenolic or synthetic resin, dried and cut to proper size, and molded under heat and pressure. The term synthetic resin is used here to include bearings that are also referred to as composition, phenolic, phenolic-resin, Bakelite, and Textolite bearings. Synthetic-resin bearings made their appearance in 1931 and have replaced the bronze and babbitt types of bearings on a number of mills, including some blooming mills, plate mills, bar and billet mills, and structural mills. The heat conductivity of such bearings is very low; heat generated must be removed continuously. This is accomplished when using water lubricated phenolic bearings by exposing much of the surface of the journal or neck to abundant sprays of water. Where the load and speed are insufficient to create frictional heat beyond a safe operating temperature, grease without water has been used successfully. Oil lubrication, using a drip feed, has the same limitations as grease, however when it is circulated as with babbitt bearings a distinct cooling effect is accomplished and results approaching those as satisfactory as when water is used, are obtained. Grease, when used in conjunction with water, has improved operating conditions on many installations where the loads are extreme and speed very low. Synthetic bearings may also be lubricated by soluble oil solutions. Additional lubrication of water-lubricated synthetic-resin bearings may be provided by shots of water-soluble oil at intervals of about 20 minutes, timed by an automatic device.

Bearings of lignum-vitae and hard wood, with water as a lubricant have been used successfully for certain mills.

The advantages of non metallic bearings include longer life, freedom from oil or grease lubrication and reduced power requirements compared to certain other types. Tabulated below is an analysis of the values of the coefficient of friction published for several types of bearings as presented by Underwood (1). These averages are subject to various considerations involving difficulties of measurement, comparability of results, etc.

Type of Bearing	Coefficient of friction	Remarks
Roller	0.0024	Practically Constant
Fluid-film	0.003	Practically Constant
Synthetic resin or fabric	0.009	Vary Considerably with
Babbitt (Good Lubrication)	0.06	effectiveness of
Bronze	0.05 - 0.15	lubrication

Lubrication of accessories of rolling mills is also of interest. All working surfaces of spindles are lubricated, usually by grease, however supporting bearings of spindles are often of synthetic resin and are water lubricated. Pinions are mounted in babbitt bearings that usually are force lubricated. The gears may operate in an oil bath. Oil is sprayed continuously on the gears, drains to the bath and overflows to a return line carrying it to a tank for recirculation. Front and back roller tables in new mills are mounted in roller bearings and equipped with automatic lubrication. In older mills bronze or babbitt bearings are lubricated by hand. The roller table rolls may be driven individually, each with its own motor or

may be driven by a shaft through miter gears. Miter gears may operate in an oil bath.

The extent of lubrication operations may be better conceived by considering the lubrication system of a certain tin plate mill. This one mill has a total of 13 automatic and manual lubrication systems serving 561 bearings.

Pickling

The removal of oxide scale from certain steel products prior to further processing is an essential operation. The oxide is removed in many instances by immersing the metal in dilute water solutions of inorganic acids for periods from two minutes to 2-1/2 hours. Such practice is termed pickling. The reasons for pickling, method, acid employed, and time of pickling, depend upon the kind of product being treated.

The term oxide scale refers to the chemical compounds of iron and oxygen formed on the surface of steel at elevated temperatures during heating for rolling or during hot rolling. Hence, the oxide is also known as mill scale. Scale is composed of layers of the three oxides, FeO, Fe_2O_3, and Fe_3O_4; the layer richest in oxygen is at the scale surface and that richest in iron at the metal surface.

Necessity for Pickling

Removal of scale to the extent accomplished by pickling is necessary for cold reduction of strip, sheet, or breakdowns because such removal promotes maximum reduction with a minimum of power; assures a good roll life by preventing accelerated wear by the hard scale; and secures increased density, uniformity, and smoothness of

surface. Unless the scale is removed from the metal prior to working it, fragments of scale become embedded in the metal, making it impossible to obtain a smooth metallic finish. Removal of scale is necessary in coating operations of any steel product to permit proper alloying and adherence of metallic coatings and proper adherence of nonmetallic coatings or paint. Sheets or rods drawn for pipe or wire production must be free of scale to prevent damage to the dies by the hard scale; which damage in turn destroys surface smoothness of the finished product. Where surface requirements of semi-finished products or bars are severe and even light defects must be removed, pickling may be employed for the purpose of removing the scale on the outside surface so that defects will be exposed. Pickling of bar and sheet products may be performed to prepare the product for ultimate end use where, for reasons of appearance or difficulties in fabrication, scale is objectionable. Pickling is also used, though to a much lesser degree, to remove the slow-forming red rust that develops on steel products after long exposure to air.

Acids Employed

Numerous acids are employed, individually and in combination, including: sulfuric, hydrochloric, nitric, hydrofluoric, and phosphoric; but sulfuric acid accounts for over 90 percent of the tonnage pickled. When the scale on some types of steel is unusually dense, adherent or insoluble, nitric or hydrofluoric acid is used in the bath in conjunction with either hydrochloric or sulfuric. Very high-alloy steels, such as the stainless group, cannot be pickled successfully in sulfuric acid solutions alone. Consequently mixtures of

sulfuric, hydrochloric, and nitric acids and mixtures of hydrofluoric and nitric acids are generally used. After pickling certain steels containing small amounts of copper or nickel in sulfuric acid, a dark film appears on the metal surface; as a rule a dilute solution of hydrochloric acid must be used to attain the necessary cleanliness.

Generally, hydrochloric acid produces a cleaner, brighter surface than sulfuric but is more expensive. Pickling in hydrochloric acid produces less acid brittleness than pickling in sulfuric, and also more objectionable in other respects than the latter, hence is seldom used for ordinary cleaning. Cold muriatic acid (HCl) often is used in small shops to pickle steel preliminary to coating and does so very efficiently. Sulfuric acid is commonly used in similar large-scale operations. Other acids are not used as commonly, although phosphoric acid is finding wider usage where a phosphate coating is desired adjacent to the steel base. For cleaning prior to galvanizing or tinning, hydrochloric acid is superior to sulfuric, and is universally used for these purposes. In the galvanizing process, sulfuric acid pickling is usually followed by a hydrochloric acid dip just preliminary to entry of the product into the flux box of the galvanizing machine. Sulfuric acid pickling may be omitted and the usual hydrochloric acid dip only used, when manufacturing corrugated galvanized roofing stock from a cold-reduced base of deoxidized annealed material which is substantially free from scale. Following sulfuric acid pickling of steel for tinning, the pickled base is stored in a tank containing 0.10 percent hydrochloric acid solution until ready for tinning. When pickled sheets are furnished the customer for use in

that condition, it is necessary to force-dry them to minimize rusting. Preliminary to drying, such pickled sheets are often given a short hydrochloric acid bath.

Some sheet galvanizers use sodium nitrate additions to the sulfuric acid pickling solution. The sodium nitrate forms nitric acid which etches steel very rapidly.

To increase speed of pickling or to increase the capacity of pickling equipment, electrolytic pickling is sometimes employed. In electrolytic pickling the regular sulfuric acid bath is used as an electrolyte to conduct current between the electrodes and the products being cleaned. For electrolytic pickling of stainless steel, phosphoric acid solutions are often employed. Some stainless steel pickling is accomplished by using either cold sulfuric acid or nitric acid.

Chemistry of Pickling

The reaction occurring when steel or iron materials are immersed in dilute inorganic acid solutions includes the solution of metal as a salt of the acid. There is considerable difference of opinion as to what actually takes place as the iron oxide is removed. In sulfuric acid pickling one theory proposes that the scale or oxide layer is relatively less soluble than the iron and bonding material underneath. The acid solution, passing through tiny cracks or fissures in the scale, reacts with the bonding structure or with the base metal itself. In this reaction hydrogen gas is liberated which, it is claimed, dislodges the scale particles. FeO is not dissolved as readily as the steel, but does have higher reaction rates than Fe_2O_3 and Fe_3O_4, both of the latter being soluble very slowly in the acid. The iron dissolves as ferrous sulphate. Another theory holds that there is an electromotive force between the

steel surface and the oxide which in the presence of an electrolyte (the acid) brings about the solution of iron from the metal surface. As solution of the bond is completed the scale drops off. There are other theories.

Unlike the black scale, the red rust (which is a hydrated sesquioxide of iron of the general formula XFe_2O_3, $Y\ H_2O$ or a double compound of ferric oxide and ferric hydroxide, $Fe\ O \cdot 2Fe\ (OH)_3$), is readily soluble in sulfuric acid, and under the conditions of pickling this action results in the formation of iron sulphate.

Ferrous sulfate remains in solution, and as concentrated acid is added from time to time, to replace that neutralized, the solution eventually becomes saturated with the sulphate to such an extent that further satisfactory pickling cannot be accomplished. Iron sulphate retards the removal of scale, and in addition, forms a scum on the pickled steel that holds particles of scale and dirt to the metal.

Certain organic chemicals called inhibitors are added to pickling solutions for the purpose of inhibiting or retarding acid activity upon the metal itself with minimum effect upon action removing the scale. Acid consumption, attack on the metal, and production of soluble metal salt are reduced by use of inhibitors. The inhibiting action is generally explained by the electrolytic theory of corrosion. Many different substances are used for inhibitors including natural vegetable or organic matter and more complex organic compounds.

Wetting agents often are added to pickling and rinsing tanks to lower interfacial tension between the steel and the liquid thereby improving wetting and rinsing of the surface. Foaming agents are sometimes used to create a foam blanket which prevents escape of acidic vapors.

Mechanics of Pickling

Considerable variation in type of pickling equipment and operation occurs in the industry. The type of product is an important factor. Pickling of steel sheets, plates, and other light gage sheared lengths, tubes, bars, and coiled rod is usually accomplished by batch pickling. Batch pickling in vats is the simplest form. The equipment consists of a minimum of two and more often three tanks. The system functions as follows: the first tank is used for the acid solution; the second contains water for rinsing the steel following removal from the pickling bath; and the third tank contains an alkaline water solution for neutralizing any remaining acid. In other arrangements the second tank may contain a more dilute acid solution or a cold water rinse; and the third tank a hot water rinse. Agitation of either the work product or the bath is generally practiced for purposes of increasing the pickling rate, reducing acid consumption, and reducing iron losses.

The tanks may be located in line and served by an overhead traveling crane or may be located at 90° intervals around a central rack-handling mast. The central mast of the latter arrangement is topped by a four-armed spider from which are hung racks holding the product to be pickled. The racks are loaded at one station, then the mast is rotated 90°, and lowered into the first vat. After a time in the first vat the racks are raised and rotated another 90° and lowered into the second vat and so on. The four arms each carry a holding rack so that as new material is being lowered in the first tank the next arm lowers pickled product into the second, the third lowers its rack into the rinse tank, and the fourth arm is in position for unloading and reloading. The product flow thus

assumes a more or less continuous aspect.

In pickling strip, preliminary to cold rolling, the strip is moved continuously through the pickling process. This operation is performed in a continuous pickling line in which there is a continuous counter current flow of pickling solution and steel. The ends of coils of strip are welded together as they are fed to the pickler. The pickling zone consists of several tanks located in a series, comprising an effective immersion length of about 250 to 300 feet. Most lines have three to five tanks, but some modern lines have only one long tank, divided into four or five sections by weirs. Following the acid tank are rinsing tanks consisting of a cold water rinse and a hot water rinse.

The operation of one modern mill is described subsequently so that the process is better understood. This mill has seven tanks, four containing acid and three for rinsing which are numbered in line 1 through 7. The strip enters tank number 1 and passes progressively through the four acid tanks and then the three washing tanks. Acid is added to tank 4 and flows countercurrent to the steel to tank 3, to tank 2, and then to tank 1 from which the waste liquor is continuously discharged. Water for diluting the acid enters tank 5 and rinses acid from the product in tank 5 before flowing into tank 4 to dilute the acid make-up. The steel is further freed of acid in tank number 6 which is a cold water rinse tank. The final tank, number 7, is a hot water rinse tank. Acid and water are added continuously at a prescribed and carefully controlled rate to the acid portion of the line, the acid to tank 4 and the water to tank 5. Usually about 35 to 50 pounds of acid is used per ton of steel pickled.

Variables in Pickling Practice

Variables in pickling practice include, among others, acid concentration, temperature and time in bath. The product being pickled is the chief factor in the variations.

Temperature of the pickling bath has a pronounced effect upon rate of pickling, in fact for each rise of 15° to 20° F the pickling rate doubles. Consequently most pickling is done at elevated temperatures. For reasons of obtaining fuel economy and of avoiding decomposition of inhibitors, temperatures are usually maintained between 150° and 190° F.

Factors influencing the acid concentrations employed are: kind of acid, time in bath, and the amount of pickling required to prepare the surface for the succeeding process. Because of the short period of time the strip is in the vat of continuous picklers, it is necessary to use relatively high concentrations of sulfuric acid. Concentrations between 12 and 25 percent are usually used in the strongest vat of continuous picklers. Vat pickling of ordinary steels is accomplished in sulfuric acid concentrations of from 5 to 12 percent. For pickling to remove light oxides from box annealed steel to be tin plated (termed white pickling), concentrations of sulfuric acid of 2 to 6 percent are employed. The concentrations of other types of acids used in pickling differ from those given for sulfuric; for example hydrochloric acid can be used in concentrations from 5 to 50 percent.

The length of the period for pickling of hot rolled plates and sheets for final end use, including rinsing time, may be as low as 6 to 10 minutes. Pickling of heavy steel shapes for purposes of surface inspection and conditioning is accomplished in about 45 minutes.

Such pickling of alloy steels may require up to 2½ hours. Some mills pickling for galvanizing of deoxidized annealed material employ only a wash pickle of from 3 to 8 minutes. In general howeverin pickling annealed stock the practice is to pickle for 8 to 20 minutes. Hot rolled material for galvanizing requires a longer pickling time, such as 20 to 45 minutes. White pickling before tinning may require only 2 to 4 minutes.

Volume and Character of Wastes

Wastes from rolling mills include (1) roll cooling water, (2) descaling water, (3) bearing lubrication losses, (4) lubricant coating wash water, (5) waste pickle liquor, and (6) miscellaneous cooling water. In general, roll cooling water, descaling water, and bearing lubrication losses combine at their source; therefore they are considered as one waste in the following discussion.

Roll Cooling, Descaling, and Bearing Lubrication Wastes

Standard practice in rolling mills is the directing of sprays of water on rolls and bearings and the circulation of water through bearing housings. This operation has three purposes, namely, to maintain proper temperatures, to flush away scale, and to lubricate synthetic resin and lignum vitae bearings. Temperatures must be maintained relatively low in order to prevent excessive wear and abrasion of roll surfaces and to minimize destruction of lubricants. Scale is loosened from the steel surfaces during rolling and unless removed increases wear on rolls and results in rough surfaces on the products. The cooling water sprayed on the rolls not only serves a cooling function but flushes away loose scale from the rolls and the product. In addition to the water sprays

used for cooling, certain mills utilize extremely high pressure sprays for the purpose of loosening and removing scale. Such descaling sprays have been described in the process section.

The water from these three sources falls to a liquid waste collecting trough which underlies the line of equipment. This liquid waste collection system terminates in a basin which is referred to as the scale pit. Scale pits are sedimentation chambers in which the more readily settleable particles of scale settle from the water. The order of the dimensions of scale pits is shown by those at two plants observed (2). The scale pit at a strip mill was 13 feet wide and 60 feet long; a blooming mill scale pit was 20 feet wide and 40 feet long. The depths of water and sediment in scale pits is generally between 10 and 20 feet.

Material settling from the water in scale pits is periodically dredged from the pit and returned to the blast furnace department for recovery of the iron.

There is considerable oil contained in these wastes. The sources of this oil are: (1) lubrication of roll bearings, pinions, spindle bearings, bearings of auxiliary equipment, and (2) washing of oil coatings from products. Oil and grease which leaks from bearings or passes through seals, is carried to waste with the roll cooling water. Soluble oil and water, or grease and water, may be used for lubricating some bearings; grease or soluble oil used in this manner enters the wastes. Hydraulic equipment utilizing oil as the pressure transfer medium is employed extensively in the shears and other mill equipment. Leaks, spills, and breaks in the oil handling equipment account for appreciable intermittent oil losses. In addition, oil in the lubrication system supply tanks is often centrifuged to remove water and

other fouling material. The rejected material contains some oil.

Lubricant coating wash water, a major contributor of oil, is discussed in a subsequent section.

Data on the volume of the wastes and their content of suspended solids and oil are presented in Table 1. These data were obtained during surveys conducted by the Public Health Service (2). They are for the effluent from scale pits. In general, the retention time in scale pits and the inlet and outlet construction are not such that optimum sedimentation is obtained. The data are net values, deductions having been made for quantities contained in the water supplies.

The data on oils are those obtained from sampling the wastes for oil. Usually there was good agreement between oil use quantities as indicated by long-time purchasing records and oil make-up data, and the amounts found in the wastes. This was true of both those mills having bearing lubrication only and those with lubricant coating wash wastes.

These wastes do exert an appreciable biochemical oxygen demand. The organic material exerting such demand is the oil. Limited results indicate that the 5 day BOD concentration in the wastes is about 50 percent of the content of oil.

The footnote of the table calls attention to the use of synthetic bearings because the use of such bearings, if exclusively water lubricated, reduces oil use and, consequently, results in lower oil concentrations in the wastes.

Variations in quantity of oil and suspended solids would be expected among mills rolling different products for the reason that equipment, operations, and product handling is considerably different.

TABLE 1 - ROLLING MILL LIQUID WASTE VOLUME AND POLLUTIONAL CONSTITUENT QUANTITIES PER TON OF STEEL PRODUCT

Roll Cooling, Descaling, and Bearing Lubrication Wastes

Type of Mill	Flow, gallons	Suspended Solids, pounds	Oil, pounds	Iron as Fe, pounds	Rolling Accomplished
Blooming Mill	630	1.0	0.23	0.38	Ingots to blooms
Slab-Bloom Mill	1030	0.67	0.74		Ingots to slabs or blooms
Billet Mill	660	1.0	0.29	0.35	Ingots to billets
Hot Strip Mill	2940	3.2	0.37	1.9	Slabs to breakdowns, sheet, or light plate
Plate and Hot Strip Mill	2260	2.3	1.10		Slabs to breakdowns, sheet, or light plate
Bar Mill	3490	6.0	0.28	3.27	Billets to bars
Structural Mill	1970	0.66	0.31		Blooms to structural shapes

Roll Cooling, Descaling, Bearing Lubrication, and Lubricant Coating Wash Water Wastes

Type of Mill	Flow, gallons	Oil, pounds	B.O.D. pounds	Rolling Accomplished
Cold-Reduced Sheet Mill	1370	1.9	0.82	Pickled breakdowns to cold-reduced sheet

Waste Pickle Liquor

Type of Pickling	Acid Used	Acidity as H_2SO_4 pounds	Iron as Fe pounds	Flow, gallons
Batch Pickling of Billets (Rinse Not Included)	H_2SO_4	2.5	2.7	5.5
Batch Pickling of Bars (Rinse Not Included)	H_2SO_4	9.6	5.8	10.8
Batch Pickling of Sheets (Strong Acid Vat Dump)	H_2SO_4	3.8	4.3	6.0
Continuous Pickling of Breakdowns (Including Hot and Cold Rinse)	H_2SO_4	21.2	14	260

Some water-lubricated synthetic resin bearings used.

TABLE 2 - ROLLING MILL LIQUID WASTE POLLUTIONAL CONSTITUENT CONCENTRATIONS

Roll Cooling, Descaling, and Bearing Lubrication Wastes

Type of Mill	Susperded Solids, ppm	Oil ppm	Iron as Fe ppm
Blooming Mill	190	45	72
Slab-Bloom Mill	78	86	
Billet Mill	182	53	64
Hot Strip Mill	130	15	78
Plate and Hot Strip Mill	122	58	
Bar Mill	207	10	112
Structural Mill	40	19	

Roll Cooling, Descaling, Bearing Lubrication, and Lubricant Coating Wash Water Wastes

Type of Mill	Oil ppm	B.O.D. ppm
Cold Reduced Sheet Mill	168	72

Waste Pickle Liquor

Type of Pickling	Acid Used	Acidity as H_2SO_4 per cent	Iron as Fe per cent	Total Solids ppm	Suspended Solids ppm
Batch Pickling of Billets (Rinse Not Included)	H_2SO_4	5.6	6.0	237,000	202
Batch Pickling of Bars (Rinse Not Included)	H_2SO_4	10.7	6.5	315,000	212
Batch Pickling of Sheets (Strong Acid Vat Dump)	H_2SO_4	7.6	8.6	345,000	264
Continuous Pickling of Breakdowns (Including Hot and Cold Rinse)	H_2SO_4	0.98	0.65	30,400	103

Lubricant Coating Wash Water

A major source of oil in certain mill wastes results from washing of oil coatings from steel products. Sheet and strip is given an oil coating after pickling; usually palm oil or a mixture of palm and mineral oil is used. Before cold rolling, the oil is removed by emulsifying it with a wetting agent and washing the steel with water. Following cold reduction the sheets are again given a coating of lubricant which must be removed prior to annealing for coating operations, such as tinning and galvanizing. If not removed the lubricant film left on the steel will decompose during annealing, and leave undesirable residues of carbonaceous material. Cold-reduced strip cleaners employ detergent solutions such as caustic soda and trisodium phosphate. Electrolytic action is employed with the cleaner in some cases, particularly when galvanizing. Thorough rinsing of the steel is accomplished after cleaning. In the hot-dip tinning operation, as the sheets leave the tin bath they pass through a layer of palm oil as explained in the process section. The sheets then pass through a hot water solution of soda ash or trisodium phosphate to remove the palm oil. In most tinning plants the washing solution is recirculated from a central storage tank. Overflow from this tank is wasted. Palm oil is recovered from the recirculated solution storage tank.

Data available concerning this waste are for the total wastes of a mill. These wastes were made up of lubricant coating wash water from washing pickled sheet, combined with cooling water from motor-generator sets, and oil coolers and wastes from the roll stands. Such data are presented in tables 1 and 2. At this mill, data on average make-up of

lubricating and coating oil indicated that 88 percent of the oil in the wastes originated in the coating operation. Such figures indicate that the lubricant coating wash water contributes to the wastes of a cold-reduced sheet mill 1.76 pounds of oil per ton of steel processed.

These wastes do not contain appreciable quantities of suspended solids because the scale has been removed in the pickling operation. The oil exerts considerable biochemical oxygen demand.

Waste Pickle Liquor

In the pickling of steel with sulfuric acid the solution eventually reaches a state in which its rate of reaction is no longer sufficient for effective pickling even though considerable acid is present in the solution. The cause of this reduction of activity is the accumulation to the point of saturation of ferrous sulphate in solution in the bath. In addition to retarding the pickling, high concentrations of ferrous sulphate in the pickling bath cause a deposit of gelatinous film on the pickled product which is objectionable for further processing.

It is usually considered good practice to permit build-up of ferrous sulphate to about 25 percent (9.2 percent iron) and work the bath until the acid content is reduced to less than 5 percent. However these figures are only generalities; there is apparently great variation in the content of acid and iron in waste pickle liquor. Data on pickling liquor gathered in field studies of the Public Health Service (2) are presented in Tables 1 and 2.

The product of hydrochloric acid pickling, ferrous chloride, is quite soluble and forms practically no objectionable scum on the metal. Consequently, satisfactory hydrochloric acid pickling can be accomplished

until the concentration of iron in the bath reaches about 18 percent.

Miscellaneous Cooling Water

Motors sufficiently large to deliver as much as 7000 or more horsepower are used to drive rolling mills. Water is used for cooling purposes in conjunction with these motors and associated equipment. This water would not be expected to receive any pollution material from this use. Where steam power is employed, there may be mill engine condensate in the wastes which will contain steam cylinder oil.

Slabs, blooms, and billets are moved through reheating furnaces by being pushed progressively forward on water-cooled skids. This use of cooling water would likewise not be expected to increase the content of pollutional materials.

Pollutional Effect

One of the objectionable features of liquid wastes from rolling mill descaling and roll cooling operations is their content of suspended solids. In the receiving water, the suspended material settles out and thus forms a continuously renewed coating of inorganic material on the bottom of the lake or river. Such deposits are destructive to bottom organisms which constitute an important source of fish food. The suspended solids are, very largely, scale particles which impart to the waste a deep gray to black appearance. This color and turbidity persists even after removal of readily settleable material by the usual settling practice. Such color and turbidity will be found objectionable from aesthetic considerations and for recreational uses of the water.

Oil is a serious deterrent to subsequent domestic or industrial use of the receiving water, possibly necessitating special treatment

for its removal. Waters used for domestic water supplies may be made objectionable due to tastes and odors caused by oil. Oil may cause difficulties at water-purification plants by coating filters and other equipment. Oil may appear as free oil, soluble oil, emulsified oil, or as a coating on suspended matter. Floating oil even in small amounts, is easily detected because of the iridescent sheen it causes on the water surface. As little as 25 gallons of oil per square mile may be visible under most favorable light conditions. Such floating oil is aesthetically offensive and may render the water useless for bathing and recreational uses. Oil coatings may be formed on objects the water contacts. Oil coatings on hulls of pleasure boats will be found offensive and may damage hull paint. Oil coatings on water front structures, piers, piling, and ships' hulls are objectionable and may constitute a fire hazard. Oil coatings on beach sands will destroy their recreational use value. Light films of oil are likely to accumulate in backwaters, slow-moving threads close to the stream banks, and on quiescent or pool surfaces of the stream thereby intensifying the problem in these areas. Wildfowl become disabled if their feathers become sufficiently saturated by contact with floating oil and will subsequently die from hunger, exposure, or drowning. Oil coatings on water surfaces reduce rearation of waters unsaturated with oxygen. The oil discharged as a coating on suspended matter may blanket the stream with an oily sludge. With agitation due to high flows this accumulated sludge may release some of the oil to the surface as floating oil.

The waste from acid pickling of steel products contains considerable iron in solution. The Public Health Service standards for drinking water state that the content of iron and manganese together preferably

should not be in excess of 0.3 p.p.m. At all but very low pH's, iron is almost insoluble, hence the iron will tend to precipitate in the receiving water. A considerable quantity of the insoluble precipitate may remain in colloidal suspension for extensive periods unless conditions for coagulation prevail. If allowed to enter a water supply, the precipitate may travel into the distribution system. The resulting deposition in pipes reduces flow capacity and adds a red color and turbid condition to the water when flushed out. The iron precipitate stains fixtures and clothing, darkens tea or vegetables, and may give the water a metallic taste. Water for textile manufacture may require less than 0.1 p.p.m. iron content, and water for rayon manufacture must necessarily have less than 0.01 p.p.m. iron.

The acid content of the pickling waste may lower the pH of the receiving waters to a point which would detract from their subsequent use, render the waters corrosive, or be destructive to aquatic life.

REMEDIAL MEASURES

Ways and means of reducing the pollutional characteristics of the wastes are discussed in this section. Process modifications as well as waste treatment methods are included. The discussion is divided into four sections according to the subjects: (1) Roll Cooling, descaling, and bearing lubrication wastes, (2) lubricant coating wash water, (3) Furnace and motor cooling water, (4) Waste pickle liquor.

Roll Cooling, Descaling, and Bearing Lubrication Wastes

Waste Treatment

Scale pits are universally employed for recovery of the scale from this waste. Scale pits are generally not of capacity and not so

designed that conditions for good sedimentation prevail. For this reason, scale pit effluents contain appreciable suspended material which can be removed by further and more efficient sedimentation. Three plants are known to provide more efficient sedimentation treatment for the wastes than the usual scale pit; an adjunct to settling of this waste is oil skimming. In all three cases the treatment is provided so that the effluent may be reused as discussed under the next sub-heading.

One treatment plant consists of a rectangular sedimentation basin providing about 10 minutes retention followed by an aeration system to aid in oil removal and finally a circular sedimentation basin providing 35 to 40 minutes detention. Oil is skimmed from both basins. Another mill uses circular clarifiers in which settleable material gravitates to the bottom then is removed by rotating sludge collectors, and oil rises to the surface and is skimmed off.

Sedimentation treatment for improvement of plant discharge is practiced at one mill. The wastes so treated are combined rolling mill and blast furnace gas wash wastes. Oil skimming is also provided. The treatment unit consisted of long earth basins providing, by dye test, about 45 minutes detention. Suspended solids were reduced on the average from 249 to 44 ppm and oil 32 to 7 ppm.

Coagulation of these wastes by chemical additions would be possible. One plant has provided equipment for adding chemicals as it enters the clarifier but it is not used. (2)

In connection with more efficient scale pits, attention is called to the general practice, especially in slab and blooming mills, of returning a large proportion of the scale pit effluent to the head of

the drain troughs under the line of equipment. The purpose is to provide a large volume of water flowing swiftly through the trough to the scale pit in order to carry along large pieces of scale which are too heavy to be moved except by such a torrent of water. Circulation of water through the scale pit in this manner is opposed to efficient sedimentation. When this is practiced, therefore, it is apparent that optimum sedimentation treatment can be accomplished most efficiently by a two-unit system in series and not a single large scale pit, recirculation for flushing being limited to the first unit's effluent.

Segregation and Reuse

The treatment of this waste by sedimentation and oil skimming and re-circulation of all or part of the effluent for use in the rolling mill is known to be practiced in three plants. Water for descaling sprays is given additional sand filtration treatment in one plant. Water for lubrication of bearings must necessarily be free of abrasives. Likewise, it is claimed that cooling water sprays on strip and sheet on the runout tables must be free of suspended material for best surface appearance.

Elimination

Oil in the wastes can be reduced by employing water-lubricated synthetic resin or lignum-vitae bearings. This type of bearing is not always exclusively water lubricated as discussed in the process section. Synthetic bearings may be lubricated with water only, with soluble oil solution, or with water and a small quantity of grease. Owing to the small coefficient of thermal conductivity, an abundance of water is necessary for adequate cooling.

Lubricant Coating Wash Water

Waste Treatment

An obvious treatment for this waste would be an oil skimming operation in units similar to settling tanks. No data is available concerning such treatment. The use of an alkaline detergent washing solution probably creates an emulsion which might remain even after the skimming treatment. Experience in breaking oil emulsions in waste waters is limited to wastes of other industries such as oil refineries and machine shops. Some literature on this subject is listed in the references (3)(4)(5)(6).

Furnace and Motor Cooling Water

Cooling waters which do not entrain pollutional materials may be segregated in a separate system, cooled and recirculated. Two plants are known to be employing this system. Cooling of the waters before recirculation is accomplished at one plant by passing them through a large open reservoir; at the other plant, forced draft cooling towers are employed.

Where heat content is an objectionable feature in the wastes such recirculation is a solution. In addition, use of fresh water is reduced and the system lends itself to maintenance of water qualities minimizing corrosion.

Waste Pickle Liquor

Methods of alleviating the waste pickle liquor disposal problem are varied and numerous. For purposes of this discussion the methods are considered under the headings (1) alternatives to acid scale removal, (2) disposal other than to watercourses, (3) acid neutralization and iron removal treatment for discharge and (4) by-product recovery. Keeping the volume requiring treatment to a

minimum is of importance to the economics of all methods of disposal. It may be advantageous to segregate the strong liquor from rinse waters or at least to minimize dilution.

This discussion mentions only the salient features of the various methods of disposal and by-product recovery. Much of the material contained in this section, even beyond the reference credits given, has as its source published articles by Hodge (7) and Hoak (8)(9). These researchers have been engaged in a program which had its inception in 1938 and has as its objective the development of a technically and economically satisfactory process for the treatment of spent pickle liquor. This work has been carried on at Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania, under sponsorship of the American Iron and Steel Institute.

Alternatives to Acid Scale Removal

Blast Cleaning

The impingement of an abrasive substance like sand, aluminum oxide or cast iron shot can satisfactorily clean scale or rust from steel surfaces. The abrasive material may be directed against the work by air under pressure or by a mechanical apparatus using centrifugal force. All types of steel bar products and shapes can be cleaned successfully by this method. The surface finish is usually quite rough which is desirable in that it promotes adherence of some coatings and is more beneficial than detrimental in some subsequent fabrication operations.

Because the cost of blast cleaning is greater than that of

pickling, blast cleaning generally is employed only for the cleaning of the following types of products: (1) those which must have certain physical characteristics essential to subsequent processing; (2) those which cannot be cleaned satisfactorily by the pickling method after such thermal treatments as normalizing or annealing; (3) those with high alloy content whose scale cannot be removed satisfactorily by ordinary pickling methods.

The chief advantages of grit blasting are: (1) it leaves the surface of the bar with a bright metallic finish without any adhering scale; (2) it is capable of cleaning a number of types of products that cannot be cleaned successfully by pickling; (3) it does not produce such physical or chemical conditions as over-pickling, under-pickling, smudge, or pitting which may attend the pickling process, and (4) loss of metal is minimized. The disadvantages of grit blasting are: (1) only a few bars can be processed at one time in the blast machine; (2) as the grit or shot builds up with scale, the efficiency of the cleaning effect is decreased; (3) the bars are difficult to inspect for surface defects because of the peening action of the grit or shot; and (4) the cost per ton of steel cleaned is greater than the cost of pickling. (10).

Sodium Hydride Process

A descaling process using sodium hydride dissolved in a bath of fused sodium hydroxide has been used commercially for more than eight years. Its advantages are most pronounced in stainless steel pickling. An important advantage of this process is that there is no problem of waste residue comparable to waste pickle

liquor. Other advantages of the treatment include: (1) sufficient penetration to provide uniform descaling, even of all grades of stainless steel; (2) no loss of metal, as compared with as much as 3 percent or more in acid pickling; (3) no hydrogen embrittlement; (4) smoother surfaces with no pitting; (5) simple equipment; and (6) less time required than other pickling methods. The method does however require more heat input than pickling, and care must be taken to prevent the introduction of any water.

The descaling solution consists of a small percent, 1.5 to 2, of sodium hydride, dissolved in a fused sodium hydroxide bath maintained at a temperature of 700°F. Sodium hydride reduces iron oxide to metallic iron and produces sodium hydroxide. Neither the metal walls of the reacting vessel or the base metal itself is attacked; in fact, the presence of NaH decreases the corrosion of iron in fused caustic. The reduced scale adheres to the metal in the fused solution but is removed in subsequent quenching operations and steam jet cleaning. Normally a light acid pickle or dip, usually hot nitric acid, follows the descaling treatment.

Electrolytic Pickling

Electrolytic pickling may be employed where size and shape of products being pickled do not vary greatly, such as in continuous strip or sheet pickling operations. The bath may be a solution of any of the common acids and it is not heated. The article to be pickled is made the anode if some actual solution of the steel is required, or, where satisfactory, it may be made the cathode. The product may even be made alternatively anodic and cathodic, assuring

effective surface cleaning. Electrolytic pickling has the advantage of uniform and controllable pickling action by regulation of the electric current.

Electrolytic cleaning of steel in a bath of molten sodium hydroxide has been proposed.

Disposal Other Than to Watercourses

Expedient Methods

Expedient methods employed by the industry to avoid discharging the liquor into watercourses include: (1) lagooning the liquor to permit it to disappear through solar evaporation and seepage into the earth or into slag dumps; and (2) discharge of the liquor into limestone caves, deep wells, exhausted oil and gas sands, and into sand and gravel sumps. Serious objections to these methods have arisen.

Vaporization with Molten Slag

One steel company disposes of pickle liquor by evaporating it with molten blast furnace slag on the slag dump. It is reported that air pollution is not a problem even though the liquor comprises waste from sulfuric, nitric, and hydrofluoric acid pickling (9). Another method of vaporizing pickle liquor with molten slag has been proposed. In this method molten slag is poured into such a volume of liquor that most of the water is vaporized, leaving a granular mass containing 10 to 12 percent moisture (9). The product could be used advantageously as a filler for fertilizer because of the content of trace elements.

Barging to Sea

A waste containing 8.5 percent sulfuric acid and 10 percent ferrous sulphate is barged to sea and discharged 14 to 15 miles off the New York City and the New Jersey shore. A recent study of the effect of these acid wastes, both chemical and biological, revealed that no lasting undesirable effects occur in the wake of the barge except an increase in the turbidity due to ferric iron precipitation (11).

Acid Neutralization and Iron Removal Treatment for Discharge

Neutralization of the acid and precipitation of the iron may satisfy the objections to discharge of pickle liquor; such treatment, utilizing various alkaline agents, is widely practiced.

Lime Treatment

Lime is the most popular of many alkaline substances that can be used. Treatment with lime can be carried to the point sufficient to neutralize the acid only; or enough lime may be added to precipitate the iron as ferrous hydroxide and the sulphate as calcium sulphate. Where the iron is not removed it may be necessary to lagoon the neutralized liquor where there is no danger of seepage into the stream. Lime may be either high calcium or dolomitic, unslaked or hydrated. One problem of lime neutralization is disposal of the sludge produced. Information concerning the economic and technical factors in neutralization of pickle liquor with lime is found in references (8) and (9).

Lime Treatment and Aeration Oxidation

An aeration-oxidation treatment supplemental to alkaline neutralization and iron precipitation has been developed. This process has the advantage of producing minimum sludge volume and

the sludge may be filtered at remarkably high rates.

Pulverized Limestone Treatment

Pulverized high calcium limestone can be used successfully for pickle liquor treatment where adequate reaction time and effective aeration can be provided (9).

Combination Pulverized Limestone-Lime Treatment

Where the aeration period is not practical for pulverized limestone treatment, a split limestone-lime treatment process has been developed whereby the free acid is neutralized with limestone and the iron precipitated with lime slurry (8).

Granulated Blast Furnace Slag Treatment

Granulated blast furnace slag has been employed on commercial scale to neutralize the acid and precipitate iron (9). The solid product sets to a hard mass which can be utilized as a foundation for building construction. Slag is a cheap neutralizing agent.

Treatment with Domestic Sewage

Pickle liquor can be disposed of in combination with domestic sewage in treatment plants. Discharge of the liquor at a uniform rate, or preferably at a rate proportionate to sewage flow, and neutralization of the free acid is necessary. The alkalinity present in sewage can be utilized for neutralization; supplemental lime treatment may be necessary. Once the acid is neutralized the ferrous sulphate acts as a coagulant which improves primary sedimentation. Such combined treatment therefore benefits both the municipality and the industry. Because iron in sewage clogs the air-diffusion plates, this method cannot be used with the activated sludge process.

By-Product Recovery

The search for a solution to the disposal problem has been one incentive to the development or proposal of many processes for recovering useful by-products from pickle liquor. These processes have been discussed in considerable detail in articles by Hodge (7) and Hoak (8)(9). A compendium outlining the more important processes has been prepared by Hoak and a subcommittee of the Steel Industry Action Committee of the Ohio River Valley Water Sanitation Commission and published in October 1952 (12). Reference is made to the material mentioned for a presentation and brief analysis of the applicability of the various methods. The Steel Industry Action Committee of the Ohio River Valley Water Sanitation Commission propose to prepare a second manual on the subject which will present a critical evaluation of the more significant disposal processes with some appraisal of their economic potential.

The eighty-odd processes which have been developed have been classified as follows (12):

a. Copperas and lower hydrates of ferrous sulfate
b. Copperas and free sulfuric acid
c. Ferrous sulfate monohydrate and sulfuric acid
d. Iron oxide and sulfuric acid
e. Ferric sulfate and sulfuric acid
f. Iron oxide and ammonium sulfate
g. Construction material (ferrous)
h. Manganese concentrate
i. Magnesia
j. Miscellaneous processes.

General Discussion of Advantages and Disadvantages of Recovery Methods

Researchers of the Mellon Institute write that the adverse economic factors involved in the recovery processes for waste pickle liquor are most difficult to overcome. The low cost of sulfuric acid and ferrous sulfate excludes the development of an especially profitable process; however the possibility that a process can break even or show a small profit must not be discounted. The comparatively high costs for installation, equipment, maintenance, and operation, due largely to the corrosive nature of the materials being processed and to the lack of anything like adequate markets for most of the by-products recoverable, have undoubtedly been the more important retarding factors in the installation of recovery processes by the industry. Contrary to the outlook for some other recovered materials, two products, namely sulfuric acid and iron oxide, usually may be used in the steel plant itself or, as a rule, sufficient markets are available.

Objections which have been raised against the processes for recovering acid and iron oxide include high costs for installation and operation, and the requirements for continuous operation and large production. It has been stated that to be economically sound, a plant must produce a minimum of about 50 to 75 tons of concentrated acid per day (9). As no single steel mill produces enough waste pickle liquor to support a plant of this size, it would be necessary to work a cooperative acid plant to convert the monohydrate recovered in several mills comprising a steel district. The construction of a cooperative acid plant or the utilization of an existing acid plant appears logical. In view of the world wide shortage of sulfur, it may become necessary to employ more expensive methods of manufacture of sulfuric acid. If so, the economics of acid

recovery will be improved. Hoak (5) states that this is not likely to occur for quite a few years.

It has been reported that the industry has voiced objections to the use of recovered acid because of the purported accumulation of deleterious impurities in the liquor. However, the Mellon Institute workers compared the pickling action of fresh sulfuric acid with recovered acid and found, after six cycles, that there was no tendency for impurities to accumulate in the recovered acid and that it was equivalent to fresh acid as a pickling agent (7). The acid used in this test was recovered by the acetone precipitation process.

In considering the economics of the acid and iron oxide recovery processes and others, the cost of alternative measures and the interests of conservation of the natural resources should be taken into account. It is not necessary for recovery processes to pay their way entirely, for if they offer a saving over treatment methods that may be required, the net result is a lower expenditure.

Several plants are producing copperas but they are able to supply the market for this compound by utilizing only a small percent of the liquor. The process must also compete with recovery of copperas from wastes of the titanium pigment industry. A potentially greater market for iron salt coagulants exists in their use in water, sewage, and industrial waste purification. Ferrous sulfate, oxidized with chlorine or used in combination with lime and other chemicals, is a coagulant which performs over a much wider pH range than does the commonly used aluminum sulfate and is also more effective in removing color. Combination of copperas with activated silica has been reported to give

excellent results as a sewage coagulant and avoids the necessity for chlorinating the copperas. The high water content of crystallized copperas precludes shipping this compound to relatively distant points. Ferrous sulfate monohydrate has much less water consequently economics of shipping are improved.

Limitations on the market demand of iron oxide pigments also limits extensive recovery of those materials.

Changing economic conditions may make more attractive the application of proposed recovery methods at some later date.

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